

The University of Chicago

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A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

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AARON SAYVETZ

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The Kinetic Energy of Polyatomic Molecules

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The theory of rotating axes and polyatomic molecules is extended in a form applicable to linear and anomalous molecules. It is applied to a linear tetratomic molecule and to an anomalous ammonia-like molecule, to obtain, in each case, a Hamiltonian kinetic energy lacking first-order terms. A second-order perturbation calculation yields the energy of interaction between rotation and vibration for the linear molecule. The relationship to Howard's theory of ethane is also given.

INTRODUCTION

THE systematic theory of the motion of polyatomic molecules referred to moving axes has been developed by Eckart¹ for the case of nonlinear normal molecules. In this theory, the unique definition of the axes is provided by certain conditions on the coupling terms² in the kinetic energy, which were suggested by Casimir's³ study of rigid bodies in quantum mechanics. It is possible, however, to treat the interaction of rotation and vibration from a more general viewpoint, such as that considered by Welker,⁴ which is applicable to linear molecules, and to various types of anomalous molecules as well. For the purposes of application, this general theory may be specialized so that it assumes a form similar to the method of rotating axes, and for nonlinear normal molecules, is, in fact, identical with it. In illustration, the method is applied to a linear tetratomic molecule and to an anomalous molecule like ammonia.

THE GENERAL METHOD

Many polyatomic molecules are known to behave like approximately rigid bodies while still others possess only one or two degrees of internal freedom. Thus, it might be said that a general N atomic molecule consists of approximately rigid parts which may move relative to each other while the whole structure translates and rotates freely through space. Let it be assumed, for the time being, that the parts are perfectly rigid and that their relative motion is unconstrained. The system is thus in neutral equilibrium since it follows that the potential energy is identically zero. To specify the position in space of the equilibrium configuration defined in this way, fewer than $3N$ coordinates are needed, and these may be taken to be of two types: (a) six (or five) coordinates α' , whose variation describes the over-all translation and rotation of the molecule, and (b) one or more coordinates α'' which describe the gross internal motions.

The equations of transformation from cartesian coordinates,

$$x_k = F_k(\alpha_\nu),$$

¹ C. Eckart, *Phys. Rev.* **47**, 552 (1935).

² See also, H. A. Jahn, *Ann. d. Physik* **23**, 529 (1935).

³ H. B. G. Casimir, *The Rotation of a Rigid Body in Quantum Mechanics*. Dissertation, Leyden (1931).

⁴ H. Welker, *Zeits. f. Physik* **101**, 95 (1936).

$k=1, 2, \dots, 3N$; $p=1, 2, \dots, M < 3N$, are simply the equations of rigid constraint under which the motion takes place, and this will be termed the "rigidly constrained" motion. It is convenient to let the x_k represent the coordinates of an atomic particle multiplied by the square root of its mass, and to use (in this section only) the summation convention. The properties of the system, in both classical and quantum mechanics, depend upon the Hamiltonian, which is readily obtained:

$$\begin{aligned}\dot{x}_k &= (\partial F_k / \partial \alpha_p) \dot{\alpha}_p \\ 2T &= \sum \dot{x}_k^2 \\ &= \sum_k (\partial F_k / \partial \alpha_p) (\partial F_k / \partial \alpha_r) \dot{\alpha}_p \dot{\alpha}_r,\end{aligned}$$

which may be written:

$$2T = A_{pr}^{(0)} \dot{\alpha}_p \dot{\alpha}_r.$$

The Hamiltonian is then

$$2H = A_0^{pr} P_p P_r,$$

where the matrix A_0^{pr} is the reciprocal of $A_{pr}^{(0)}$, and P_p is conjugate to α_p . Since the solution of the characteristic value problem for this Hamiltonian is known in most cases, the rigidly constrained motion can be considered as part of the zeroth-order approximation to the true motion.

To secure a more accurate molecular model, the atoms hitherto supposed to constitute one of the rigid parts must be allowed to vibrate about their equilibrium positions but, as a first approximation, with very small amplitudes, so that the configuration departs only slightly from the rigid structure. If the $3N-M$ additional degrees of freedom, q_λ , are introduced in the form:

$$x_k = F_k(\alpha_p) + f_{k\lambda}(\alpha_p) q_\lambda, \quad (1)$$

$\lambda=1, 2, \dots, 3N-M$, so that they describe the deviation from equilibrium, and the zeroth-order potential energy is written as a (positive definite) quadratic form in the q_λ :

$$2U_0 = b_{\lambda\mu}(\alpha') q_\lambda q_\mu, \quad (2)$$

the motion will have the desired characteristics. Thus, Eq. (1) represents a loosening of the rigid constraints, and the motion might now be described as the "elastically constrained" motion. The solution of the "elastic constraint" problem enables the prediction of the major features of the molecule's infra-red spectrum.

As usual, the Hamiltonian must be computed. The velocities are:

$$\dot{x}_k = [\partial F_k / \partial \alpha_p + (\partial f_{k\lambda} / \partial \alpha_p) \dot{q}_\lambda] \dot{\alpha}_p + f_{k\lambda} \dot{q}_\lambda,$$

and the Lagrangian kinetic energy has the form:

$$2T = A_{pr} \dot{\alpha}_p \dot{\alpha}_r + 2B_{p\lambda} \dot{\alpha}_p \dot{q}_\lambda + C_{\lambda\mu} \dot{q}_\lambda \dot{q}_\mu, \quad (3)$$

in which the coefficients A_{pr} have the form: $A_{pr}^{(0)} + A_{pr\lambda} q_\lambda + A_{pr\lambda\mu} q_\lambda q_\mu$. The first group of terms in (3) constitutes the energy of the system under the constraints $q_\lambda = \text{constant}$, and includes the energy of translation and rotation; the third sum is the kinetic energy of vibration, while the second represents the energy of interaction between rotation and vibration.

It is desired, first, that the interaction terms be small enough to be considered as a perturbation of second order or higher, and second, that the q_λ be the normal coordinates. To see how the first requirement, which is a generalization of what has been called Casimir's condition,^{1, 3} can be effected, consider the explicit form of the $B_{p\lambda}$, which is

$$B_{p\lambda} = (\partial F_k / \partial \alpha_p) f_{k\lambda} + (\partial f_{k\mu} / \partial \alpha_p) f_{k\lambda} q_\mu,$$

or, for short,

$$B_{p\lambda} = B_{p\lambda}^{(0)} + B_{p\lambda\mu} q_\mu.$$

If, as usual, one sets

$$B_{p\lambda}^{(0)} = 0, \quad (4)$$

the $B_{p\lambda}$ will be small for small vibrations. These may be considered as equations partially determining the $3N(3N-M)$ functions $f_{k\lambda}$. Since there are M equations for each value of λ , $3N-M$ of the $f_{k\lambda}$ remain arbitrary. These are determined by the solution of the normal vibration problem in the $3N-M$ coordinates q_λ as follows. The potential energy,

$$U(x_k) = U(F_k + f_{k\lambda} q_\lambda),$$

may be expanded in a Taylor's series about the equilibrium values of the coordinates:

$$\begin{aligned}U &= \frac{1}{2} (\partial^2 U / \partial x_k \partial x_l)_{x=F} f_{k\lambda} f_{l\mu} q_\lambda q_\mu + \dots \\ &= \frac{1}{2} \beta_{kl} f_{k\lambda} f_{l\mu} q_\lambda q_\mu + \dots,\end{aligned}$$

this being a definition of β_{kl} . The $b_{\lambda\mu}$, (Eq. (2)), are therefore,

$$b_{\lambda\mu} = \beta_{kl} f_{k\lambda} f_{l\mu},$$

while the $C_{\lambda\mu}$, (Eq. (3)), are readily verified to be

$$C_{\lambda\mu} = f_{k\lambda} f_{k\mu}.$$

The remaining $f_{k\lambda}$ are then uniquely determined by the conditions:

$$b_{\lambda\mu} = 0 \quad (\lambda \neq \mu), \quad (5)$$

$$C_{\lambda\mu} = A_{\lambda}(\alpha_p) \delta_{\lambda\mu}, \quad (6)$$

where the A_{λ} are any preassigned functions.

The explicit definition of the α_p depends on the particular type of molecule to which the method is to be applied, and for this purpose, normal and anomalous molecules may be distinguished, and discussed separately.

NORMAL MOLECULES

A molecule which, in the vibrationless state (neglecting zero-point energy), behaves like a completely rigid body may be called normal. If it is nonlinear, the α_p are six in number ($M=6$), and are most conveniently chosen to specify the position in space of a set of axes moving with the molecule, namely; the three components, X, Y, Z , of the vector $\mathbf{R}$ to the origin, and the three Eulerian angles,⁵ θ, ϕ, ψ , of the axes. Let the unit vectors along the moving axes be $\mathbf{e}_i$ remembering that these are functions of the Eulerian angles. Also, let the index k of Eq. (1) be an abbreviation for two indices, i, a , ($i=x, y, z; a=1, 2, \dots, N$), so that x_{ia} are the coordinates of the a th atom in fixed axes. If $\mathbf{e}_i$ are the fixed unit vectors, the rigid constraints, $F_k(\alpha_p)$, become

$$F_{ia} = m_a^{\frac{1}{2}} (\mathbf{R} + \mathbf{z}_a) \cdot \mathbf{e}_i,$$

where $\mathbf{z}_a (= \sum_i z_{ia} \mathbf{e}_i)$ specifies the equilibrium position of the a th atom in the moving axes.

It will now be shown that, for this case, the method can be reduced to the method of rotating axes. Adopting the notation of reference 1, let the $f_{k\lambda}$ of Eq. (1) have the form

$$f_{ia\lambda} = (\sum_j z_{\lambda ja} \mathbf{e}_j) \cdot \mathbf{e}_i, \quad (7)$$

where $j=x, y, z$, and the $z_{\lambda ja}$ are constants to be

determined by Eqs. (4), (5) and (6). Eq. (1) becomes

$$x_{ia} = [m_a^{\frac{1}{2}} \mathbf{R} + \sum_j (m_a^{\frac{1}{2}} z_{ja} + \sum_{\lambda} z_{\lambda ja} q_{\lambda}) \mathbf{e}_j] \cdot \mathbf{e}_i. \quad (8)$$

If y_{ia} stands for the cartesian coordinates of the a th atom in the moving axes, multiplied by $m_a^{\frac{1}{2}}$, it is also true that

$$x_{ia} = [m_a^{\frac{1}{2}} \mathbf{R} + \sum_j y_{ja} \mathbf{e}_j] \cdot \mathbf{e}_i.$$

Hence, by comparison with Eq. (8),

$$y_{ja} = m_a^{\frac{1}{2}} z_{ja} + \sum_{\lambda} z_{\lambda ja} q_{\lambda},$$

which is the conventional transformation of coordinates. It remains to be proved that the six equations, $B_{p\lambda}^{(0)} = 0$, are precisely the ones used to define the rotating axes.

Notice, first, that for $\alpha_p = X, Y, Z$, $B_{p\lambda\mu} = 0$, so that $B_{p\lambda}^{(0)} = 0$ implies $B_{p\lambda} = 0$. But since this is the condition that the kinetic energy of translation be separable, the three equations $B_{X\lambda} = 0$, etc., must be equivalent to

$$\sum_a m_a \mathbf{r}_a = 0, \quad (9)$$

where $\mathbf{r}_a$ is the position vector in the moving axes, i.e., the origin of these axes is always at the centroid of the molecule. That the equations do have this form can also be proved. The remaining three equations may now be found. For $\alpha_p = \theta$, for example,

$$\partial F_{ia} / \partial \theta = m_a^{\frac{1}{2}} [z_{za} c'' \mathbf{e}_x - z_{za} s'' \mathbf{e}_y + (z_{ya} s'' - z_{za} c'') \mathbf{e}_z] \cdot \mathbf{e}_i.$$

In this expression, and in what follows, $s, c, = \sin, \cos \theta$; $s', c' = \sin, \cos \phi$; $s'', c'' = \sin, \cos \psi$. Thus, $\partial F_{ia} / \partial \theta$ and $f_{ia\lambda}$ (Eq. (7)) are the i th components in the fixed axes of certain vectors whose components in the moving system are the coefficients of $\mathbf{e}_i$ in the respective expressions for $\partial F_{ia} / \partial \theta$ and $f_{ia\lambda}$. Since the $B_{p\lambda}^{(0)}$ are the sums of scalar products of these vectors resolved along $\mathbf{e}_i$, they can be written in terms of the other components as well, giving:

$$B_{\theta\lambda}^{(0)} = \sum_a m_a^{\frac{1}{2}} [z_{\lambda za} z_{za} c'' - z_{\lambda ya} z_{za} s'' + z_{\lambda za} (z_{ya} s'' - z_{za} c'')].$$

On rearrangement, this becomes:

$$\sum_a m_a^{\frac{1}{2}} (s'' \mathbf{z}_a \times \mathbf{d}_{a\lambda} \cdot \mathbf{e}_x + c'' \mathbf{z}_a \times \mathbf{d}_{a\lambda} \cdot \mathbf{e}_y),$$

where $\mathbf{d}_{a\lambda} = \sum_j z_{\lambda ja} \mathbf{e}_j$. In like manner,

⁵ The definition of the Eulerian angles to be used here is that of E. T. Whittaker, *Analytical Dynamics* (Cambridge, third edition, 1927), p. 10.

$$B_{\phi\lambda}^{(0)} = \sum_a m_a^{\frac{1}{2}} (SC'' \mathbf{w}_{a\lambda} \cdot \mathbf{e}_x - SS'' \mathbf{w}_{a\lambda} \cdot \mathbf{e}_y - c \mathbf{w}_{a\lambda} \cdot \mathbf{e}_z) = 0$$

$$B_{\psi\lambda}^{(0)} = \sum_a m_a^{\frac{1}{2}} \mathbf{w}_{a\lambda} \cdot \mathbf{e}_z = 0,$$

in which $\mathbf{w}_{a\lambda} = \mathbf{z}_a \times \mathbf{d}_{a\lambda}$. These three equations imply that

$$\sum_a m_a^{\frac{1}{2}} \mathbf{z}_a \times \mathbf{d}_{a\lambda} = 0, \quad (10)$$

which is Casimir's condition in vector form,⁶ since $\mathbf{d}_{a\lambda}$ has the dimensions $m^{\frac{1}{2}} \times \text{length}$.

The normal coordinate problem may likewise be reduced to the conventional one. The $b_{\lambda\mu}$ (Eq. (2)) are simply constants and all the A_λ can thus be set equal to the same normalization constant, A .

Linear molecules

If the equilibrium configuration of the molecule is linear, only five coordinates are necessary to specify its rigid motion: X , Y , Z , θ and ϕ , and there must be $(3N-5)q_\lambda$. Hence, there are only five of the Eqs. (4), which are insufficient to define a set of moving axes uniquely. If, now, the transformation (8) is made exactly as in the preceding section, the angle ψ enters as an arbitrary parameter, which may therefore be set equal to zero, completing the definition of the axes.

The choice of the two Eulerian angles, θ and ϕ , as "rigid constraint" variables implies that $\mathbf{e}_z$ passes through the equilibrium configuration, which can always be required to have its center of mass at the origin, so that

$$\begin{aligned} z_{za} &= z_{ya} = 0 \\ \sum_a m_a z_{za} &= 0. \end{aligned}$$

In the next section, this method is applied to a general tetratomic linear molecule; the results obtained there may be of use in the interpretation of the rotational band structure of the acetylene molecule.

TETRATOMIC LINEAR MOLECULE

In order to compute the kinetic energy, the $f_{ia\lambda}$, and hence the $z_{ia\lambda}$, must be found explicitly by solving Eqs. (5), (6), (9) and (10). Written in

scalar form, Eqs. (9) and (10) are:

$$\begin{aligned} \sum_a m_a^{\frac{1}{2}} z_{\lambda ia} &= 0 \quad (i=x, y, z) \\ \sum_a m_a^{\frac{1}{2}} z_{za} z_{\lambda za} &= 0 \\ \sum_a m_a^{\frac{1}{2}} z_{za} z_{\lambda ya} &= 0, \end{aligned} \quad (11)$$

while Eq. (6), which is also invariant under a rotation of the axes, takes the form

$$\sum_a \sum_i z_{\lambda ia} z_{\mu ia} = A \delta_{\lambda\mu}. \quad (12)$$

The $3N-5=7$ linearly independent solutions of (11) can then always be chosen normalized and orthogonal so as to satisfy (12), in which A is conveniently taken to be the equilibrium moment of inertia, $\sum_a m_a z_{za}^2$. To find particular solutions, set $z_{\lambda xa} = z_{\lambda ya} = 0$; the one remaining equation has three independent solutions: $z_{1za} = g_a^{(1)}$, $z_{2za} = g_a^{(2)}$, $z_{3za} = h_a$. Two of these are also solutions for $z_{\lambda za} = z_{\lambda ya} = 0$ ($\lambda=4, 5$), and for $z_{\lambda za} = z_{\lambda xa} = 0$ ($\lambda=6, 7$). Thus, q_1 , q_2 , q_3 describe the parallel vibrations, q_4 and q_5 one perpendicular mode, and q_6 and q_7 , the other.

The potential energy must now be considered. On account of the rotational symmetry of the equilibrium configuration, and the choice of the $z_{\lambda ia}$, it must have the form:

$$\begin{aligned} 2U_0 &= \sum_{\lambda, \mu} B_{\lambda\mu} q_\lambda q_\mu + b_{44}(q_4^2 + q_5^2) \\ &\quad + b_{55}(q_5^2 + q_7^2) + 2b_{45}(q_4 q_5 + q_6 q_7), \end{aligned}$$

where $\lambda, \mu=1, 2, 3$. Since there are four non-diagonal terms, there are four of Eqs. (5), and in order to satisfy these, it is necessary to form more general solutions of (11) without altering the character of the q 's. This may be accomplished by taking separate orthonormal linear combinations of the solutions numbered 1, 2, 3, and of those numbered 4 and 5, which provides the four independent constants needed to diagonalize the potential energy. Because of the degeneracy of the perpendicular vibrations, the same combinations used for solutions 4 and 5 must be employed for solutions 6 and 7. The complete solution may therefore be written:

$$\begin{aligned} z_{\lambda za} &= \alpha_{\lambda 1} g_a^{(1)} + \alpha_{\lambda 2} g_a^{(2)} + \alpha_{\lambda 3} h_a \quad (\lambda=1, 2, 3) \\ z_{4za} &= z_{5ya} = \beta_{11} g_a^{(1)} + \beta_{12} g_a^{(2)} \\ z_{5za} &= z_{7ya} = \beta_{21} g_a^{(1)} + \beta_{22} g_a^{(2)}. \end{aligned}$$

The Hamiltonian

The Hamiltonian kinetic energy, readily computed by the method of Wilson and Howard,⁷

⁷ E. B. Wilson and J. B. Howard, reference 6.

⁶ C. Eckart, reference 1, Eq. (25), p. 556. Also, E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 261 (1936), Eq. (3).

turns out to be

$$2AT = f^{-2}[M_x - \Lambda_x]^2 + (M_y - \Lambda_y)^2 + \Sigma p_\lambda^2,$$

where p_λ is conjugate to q_λ , $\mathbf{M}$ ($= M_x \mathbf{e}_x + M_y \mathbf{e}_y + M_z \mathbf{e}_z$) is the total angular momentum about the center of mass, and

$$f = 1 + \alpha_{13}q_1 + \alpha_{23}q_2 + \alpha_{33}q_3.$$

The calculation also yields the result that

$$M_x - \Lambda_x = 0.$$

The quantities Λ are identical (except for a normalization factor) with Wilson and Howard's p_x , p_y , p_z , and are given by

$$\begin{aligned}\Lambda_x &= (1/A) \Sigma \mathfrak{X}_\lambda p_\lambda; & \Lambda_y &= (1/A) \Sigma \mathfrak{Y}_\lambda p_\lambda; \\ \Lambda_z &= (1/A) \Sigma \mathfrak{Z}_\lambda p_\lambda,\end{aligned}$$

in which

$$\begin{aligned}\mathfrak{X}_\lambda &= \Sigma_\mu \Sigma_a (z_{\lambda z a} z_{\mu y a} - z_{\lambda y a} z_{\mu z a}) q_\mu \\ \mathfrak{Y}_\lambda &= \Sigma_\mu \Sigma_a (z_{\lambda x a} z_{\mu z a} - z_{\lambda z a} z_{\mu x a}) q_\mu \\ \mathfrak{Z}_\lambda &= \Sigma_\mu \Sigma_a (z_{\lambda y a} z_{\mu x a} - z_{\lambda x a} z_{\mu y a}) q_\mu.\end{aligned}$$

Finally, the relations of M_x and M_y to the momenta conjugate to θ , ϕ , and q_λ are:

$$\begin{aligned}M_x &= -(1/s)P_\phi + (c/s)\Lambda_z \\ M_y &= P_\theta.\end{aligned}$$

It should be noted that the Λ 's, which always appear in the Hamiltonian of a rotating vibrator, are not the same as the components of the vibrational or internal angular momentum. The latter are defined as $\Sigma \mathfrak{X}_\lambda q_\lambda$, etc., rather than as $\Sigma \mathfrak{X}_\lambda p_\lambda$.

The calculation of the characteristic values of the Hamiltonian operator is entirely analogous to that performed by Weinberg and Eckart⁸ for the triatomic linear molecule, so that only the important steps will be described here.

The perturbation calculation

The approximation,

$$f = 1,$$

is equivalent to neglecting terms of third order and higher, while Casimir's condition ensures the absence of first-order terms. There remain only terms of zero and second order, and these are:

$$\begin{aligned}2AT_0 &= \Sigma p_\lambda^2 \\ T_2 &= T - T_0.\end{aligned}$$

If polar coordinates⁹ are introduced,

$$\begin{aligned}q_4 &= \rho_1 \cos \chi_1; & q_5 &= \rho_2 \cos \chi_2 \\ q_6 &= \rho_1 \sin \chi_1; & q_7 &= \rho_2 \sin \chi_2,\end{aligned}$$

the zero-order wave functions are, in Dennison's¹⁰ notation,

$$\begin{aligned}\psi_0 &= v(\theta, \phi) \psi^{V_1}(q_1) \psi^{V_2}(q_2) \psi^{V_3}(q_3) \\ &\quad \times R^{V_4 l_1}(\rho_1) e^{\pm i l_1 \chi_1} R^{V_5 l_2}(\rho_2) e^{\pm i l_2 \chi_2},\end{aligned}$$

in which $l_1 = V_4, V_4 - 2, \dots, 1$ or 0 , etc. and $v(\theta, \phi)$ is an undetermined coefficient. This can also be written:

$$\psi_0 = v(\theta, \phi) u_{ng}^N(q, \rho, \chi),$$

where N is an abbreviation for the quantum numbers V , n ranges over all the combinations $l_1 l_2$, and g may have the values $++$, $+-$, etc. The zero-order energy,

$$W_0^N = \Sigma_i (V_i + \frac{1}{2}) \hbar \omega_i + (V_4 + 1) \hbar \omega_4 + (V_5 + 1) \hbar \omega_5,$$

is therefore of weight $\pi_n = (V_4 + 1)(V_5 + 1)$. In this and all following summations in this section, the index i has the range $1, 2, 3$. Since the first-order energy corrections, W_1 , due to the addition of cubic terms in the potential energy, are all zero, the degeneracy is unaltered to this approximation, and the correct zero order combinations for the second-order calculation are

$$\Sigma_n \Sigma_g v_{ng} u_{ng}.$$

If the operators T are defined by

$$T_{ng}{}^{n'g'} v = \int u_{n'g'}^* T_2 v_{ng} u_{ng} dq_1 \cdots dq_7,$$

the secular equations have the form:

$$\Sigma_n \Sigma_g T_{ng}{}^{n'g'} v_{ng} = W'' v_{n'g'},$$

in which W'' is that part of the second-order energy correction, W_2 , arising from T_2 alone. This "separability" of W_2 is possible only because the matrix elements of the first-order potential energy have the property:

$$(U_1)_{ng}{}^{mh} = 0 \quad (mh \neq ng),$$

where mh has the same significance as ng but

⁹ The operators must be transformed correspondingly: $p_4 = \cos \chi_1 p_\rho - \rho^{-1} \sin \chi_1 p_\chi$, etc.; Λ_z becomes simply: $p_{\chi_1} + p_{\chi_2}$.
¹⁰ D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

⁸ A. Weinberg and C. Eckart, J. Chem. Phys. **5**, 517 (1937).

refers to a wave-function for any state other than W_0^N . The kinetic energy operators themselves have the form:

$$T_{n\theta}^{n'\theta'} = T_{n\theta} \delta_{n\theta, n'\theta'}$$

and are

$$T_{\pm\pm} = (1/2A) \{ s^{-1} P_\theta s P_\theta + s^{-2} [P_\phi - \hbar c(\pm l_1 \pm l_2)]^2 \} + C.$$

The characteristic values are immediately available:

$$W'' = (\hbar^2/2A) [J(J+1) - K^2] + C,$$

where $K = (\pm l_1 \pm l_2)$, $J = |K|$, $|K| + 1, \dots$. The first part is essentially the energy of a linear symmetric top, while the energy of interaction is

$$C = (\hbar^2/2A) \{ (V_4 + 1) \times [\Sigma r_i^2 (V_i + \frac{1}{2}) (\omega_i/\omega_4 + \omega_4/\omega_i)] + (V_5 + 1) [\Sigma t_i^2 (V_i + \frac{1}{2}) (\omega_i/\omega_5 + \omega_5/\omega_i)] - 2 \},$$

in which the integer 2 appears because there are two degenerate perpendicular vibrations, and

$$r_i = \alpha_{i1}\beta_{11} + \alpha_{i2}\beta_{12} \\ t_i = \alpha_{i1}\beta_{21} + \alpha_{i2}\beta_{22}.$$

This is analogous to Weinberg and Eckart's result for the triatomic case, and the generalization to an n atomic linear molecule is obvious.

For the symmetric molecule X_2Y_2 , the following simplifications occur:

$$r_1 = 1; \quad r_2 = r_3 = 0 \\ t_1 = 0; \quad t_2 = -(1 - t_3^2)^{1/2}.$$

Thus, one constant, in addition to the normal frequencies, remains to be determined by the potential energy.

ANOMALOUS MOLECULES

These are molecules possessing internal motions with amplitudes too large to be treated as normal vibrations, as, for example, the free internal rotation of an ethane-like molecule. Another example, to be discussed here, is a model of the ammonia molecule, in which it is supposed that the nitrogen atom, in an excited vibrational state, can surmount a relatively low potential barrier and vibrate between two extreme positions on opposite sides of the plane of the hydrogen atoms.

YX_3

The rigidly constrained configuration, YX_3 , is taken to be a tetrahedron of variable height with the Y nucleus at the apex, on the z axis of a moving system of axes, while the X nuclei form an equilateral triangle parallel to the x - y plane. The anomalous coordinate, $\alpha'' = z$, is thus the z coordinate of the Y atom. The remaining coordinates are, as before, the three cartesian coordinates of the origin, three Eulerian angles, and five normal coordinates.

If the X nuclei, of mass m , are numbered 1, 2, 3 and the axes are the principal axes of the equilibrium configuration, the vectors $\mathbf{z}_a$ are:

$$\mathbf{z}_1 = -(S/2)\mathbf{e}_x - (\sqrt{3}/6)S\mathbf{e}_y - (M/3m)z\mathbf{e}_z \\ \mathbf{z}_2 = (S/2)\mathbf{e}_x - (\sqrt{3}/6)S\mathbf{e}_y - (M/3m)z\mathbf{e}_z \\ \mathbf{z}_3 = (\sqrt{3}/3)S\mathbf{e}_y - (M/3m)z\mathbf{e}_z \\ \mathbf{z}_4 = z\mathbf{e}_z,$$

where M is the mass of the Y nucleus, and S represents the side of the equilateral triangle. Note that the lengths of the $\mathbf{z}_a$ are not constant, as for a normal molecule, but vary with the time.

The position vectors for the elastically constrained motion are given by

$$\mathbf{r}_a = \mathbf{z}_a + m_a^{1/2}\delta_a,$$

where δ_a , the mass-adjusted displacement from equilibrium, is defined as

$$\delta_a = \Sigma_\lambda q_\lambda \mathbf{d}_{a\lambda} \\ = \Sigma_j \Sigma_\lambda z_{\lambda ja} q_\lambda \mathbf{e}_j.$$

Finally, the seven equations, $B_{\mu\lambda}^{(0)} = 0$, may be written:

$$\Sigma m_a^{1/2} \delta_a = 0 \\ \Sigma m_a^{1/2} \mathbf{z}_a \times \delta_a = 0 \\ \delta_4 \cdot \mathbf{e}_z = 0. \quad (13)$$

The seventh equation states that no normal vibration involves motion of the Y atom along the z axis, or that all $z_{\lambda z4} = 0$.

The potential energy,

$$U = U(q_1 \cdots q_5, z),$$

when expanded about the point $q_\lambda = 0$, $z = z$, takes the form:

$$U = U(z) + \Sigma_\lambda \Sigma_\mu b_{\lambda\mu}(z) q_\lambda q_\mu + \cdots$$

This assumes that for $q_\lambda = 0$, the X atoms are in equilibrium for all values of z , which is, of course,

an approximation. The normal vibrations are given by the five orthonormal solutions of (13) which diagonalize the quadratic part of the potential energy. Three of these, ($\lambda=1, 2, 3$), are identical with the normal vibrations of three equal atoms at the corners of an equilateral triangle, the Y atom being unaffected. The coefficients describing the remaining double vibration, ($\lambda=4, 5$), are:

$$\begin{aligned} z_{4xa} &= z_{5ya} = 0 \\ z_{4ya} &= z_{5xa} = -(1/3)(M/m)^{1/2}d \quad (a \neq 4) \\ z_{4y4} &= z_{5x4} = d \\ z_{4z1} &= z_{4z2} = -\frac{1}{2}Kdz \\ z_{4z3} &= Kdz \\ z_{5z1} &= -z_{5z2} = -(\sqrt{3}/2)Kdz \\ z_{5z3} &= 0, \end{aligned}$$

where K is a constant, but d is a function of z determined by the requirement that the normalization factor be independent of z . What is sometimes referred to as the sixth "normal vibration," namely; the z motion of the Y atom, is determined by $U(z)$. Furthermore, since the amplitudes of some of the other vibrations depend on z , this variable enters the interaction terms of the kinetic energy in a rather complicated manner. If the experimental data warrants it, it would be interesting to investigate the contribution of such terms to the energy levels.

Hamiltonian kinetic energy

It is now possible to calculate the second-order terms in the Hamiltonian of our model with complete generality. The Lagrangian kinetic energy is:

$$2T = \sum m_a (\dot{\mathbf{R}} + \dot{\mathbf{r}}_a)^2$$

and

$$\dot{\mathbf{r}}_a = \boldsymbol{\omega} \times \mathbf{r}_a + \dot{\mathbf{z}}_a + m_a^{-1} \dot{\mathbf{d}}_a.$$

Taking account of Eqs. (13) and their time derivatives, and neglecting terms quadratic in q_λ , since these give rise to terms of third or higher order, one gets:

$$\begin{aligned} 2T = \sum_i \sum_j I_{ij} \omega_i \omega_j + 2\omega_x (\sum \mathfrak{X}_\lambda \dot{q}_\lambda + R_1 \dot{z}) \\ + 2\omega_y (\sum \mathfrak{Y}_\lambda \dot{q}_\lambda + R_2 \dot{z}) + 2\omega_z (\sum \mathfrak{Z}_\lambda \dot{q}_\lambda \\ + \mu M \dot{z}^2 + A \sum \dot{q}_\lambda^2, \end{aligned}$$

in which the I_{ij} are the instantaneous moments and products of inertia, and

$$\begin{aligned} \mu &= (M/3m) + 1 \\ R_1 &= 2\mu M^{1/2} d q_4 \\ R_2 &= -2\mu M^{1/2} d q_5. \end{aligned}$$

Notice that the zero-order term in z , which is separable, involves μM rather than M .

The Hamiltonian kinetic energy takes the form:

$$2T = \sum_i (M_i - \Lambda_i)^2 / I_i^\circ + P_z^2 / M\mu + (1/A) \sum p_\lambda^2,$$

where I° is an equilibrium moment of inertia, and depends on z . As before, $M_i = \partial T / \partial \omega_i$ and $P_z = \partial T / \partial \dot{z}$ but the Λ_i are now defined by

$$\begin{aligned} \Lambda_x &= (1/A) \sum \mathfrak{X}_\lambda p_\lambda + (R_1 / M\mu) P_z \\ \Lambda_y &= (1/A) \sum \mathfrak{Y}_\lambda p_\lambda + (R_2 / M\mu) P_z \\ \Lambda_z &= (1/A) \sum \mathfrak{Z}_\lambda p_\lambda. \end{aligned}$$

Ethane

This molecule has been studied in detail by Howard,¹¹ and it will be sufficient to mention that the equations by which he removes the degrees of freedom corresponding to "incipient translations, over-all rotations, and internal rotation" are the seven equations, $B_{p\lambda}^{(0)} = 0$, appropriate to his choice of the seven rigid constraint variables. Six of these variables are identical with those chosen here for normal molecules, as are the corresponding six equations (our Eqs. (9) and (10)); the seventh coordinate, which describes the internal motion, is taken to be the angle between the two methyl groups, considered as rotating relative to each other about a common axis, (the z axis of the moving system).

The seventh equation turns out to be:

$$\sum_a m_a \frac{1}{2} \mathbf{z}_a \times \mathbf{d}_{a\lambda} \cdot \mathbf{e}_z = 0,$$

where the summation extends over the atoms of one methyl group only. This means that, in first approximation, the z component of the angular momentum of each methyl group vanishes separately.

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¹¹ J. B. Howard, J. Chem. Phys. 5, 442 (1937); 5, 451 (1937).

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